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## UNITED STATES ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, D.C. 20460

1986

Memorandum

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

Subject:

Chlorpyrifos (Lorsban®). Amended Registration for

Foliar Application to Brassica (cole) Crop Group

Vegetables (Acc. No. 261115).

RCB #464, 465

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Dow Chemical Company U.S.A. proposes amended registrations for foliar applications of Lorsban® 4E (EPA Reg. No. 464-448) and Lorsban® 50W (EPA Reg. No. 464-552) to broccoli, Brussels sprouts, cabbage, cauliflower, collards, kale and kohlrabi to control various pests. The active ingredient in these formulations is chlorpyrifos. Lorsban® 4E is a 4 lb.a.i./gal emulsifiable concentrate (40.7% chlorpyrifos petroleum derivative solvent inert ingredients). Lorsban® 50W is a 50% wettable powder (50% chlorpyrifos; 50% inerts).

Tolerances for chlorpyrifos are currently established for a variety of agricultural commodities ranging from 0.05 ppm (snap beans, peanuts) to 15 ppm (alfalfa hay)(40 CFR 180.342). A tolerance is currently established for the crop group Brassica (cole) leafy vegetables at 2 ppm (of which, no more than 1 ppm is chlorpyrifos).

Lorsban® 4E is currently registered for use on the crop group Brassica (cole) leafy vegetables. Application rates are 1.6-2.4 fl.oz. (0.02-0.03 lb.a.i.)/1000 linear feet of row for cauliflower, and 1.6-2.75 fl.oz. (0.02-0.034 lb.a.i.)/1000linear feet of row for broccoli, Brussels sprouts, cabbage, collards, kale, kohlrabi and turnips. For direct seeded crops, specified dosages are to be applied in a water based spray as a 4 inch wide band over the row at planting time in a minimum of 40 gallons total spray per acre. For transplanted crops, Lorsban® 4E is to be applied as a water based spray directed to the base of the plants, and using a minimum of 40 gallons of spray per acre. Lorsban is not to be applied to these

vegatables as a foliar application. A maximum of 2 pints (1 lb.a.i.)/A/season may be applied to cauliflower planted in 40 inch rows (use proportional amounts for other row spacings not to exceed 4 pints (2 lb.a.i.)/A/season). A maximum application of 2.6 pints (1.3 lb.a.i.)/A/season may be applied to broccoli, Brussels sprouts, cabbage, Chinese cabbage and turnips in 40 inch rows (a maximum of 4.5 pints (2.25 lb.a.i.)/A/season for other row spacings). One application only is allowed and a 30 day PHI is specified. No restrictions are mentioned for applications to collards, kale or kohlrabi.

Lorsban® 50W is not currently registered for use on the crop group Brassica (cole) leafy vegetables.

The proposed new uses for the two Lorsban® formulations are for <u>foliar</u> applications to broccoli, Brussels sprouts, cabbage, cauliflower, collards, kale and kohlrabi.

Lorsban® 4E is to be applied as a full coverage foliar spray at the rate of l quart (l lb.a.i.)/A in 3-5 gallons of water per acre using aerial application or in 20-150 gallons of water per acre using ground application equipment. Aplications are to be made when insects first appear on the foliage and at 7-14 day intervals thereafter or as needed. A maximum of 6 applications per season could be made with a 21 day PHI imposed.

Lorsban® 50W would be applied as a foliar spray at a rate of 2 lb. (1 lb.a.i.)/A mixed with sufficient water to ensure thorough and complete coverage of the foliage and crop, and applied as a concentrate or dilute spray using conventional, power operated spray equipment. A maximum of 6 applications could be made per season (total of 6 lb.a.i./A/season) with no interval between applications specified, and a 21 day PHI would be required.

The residues of concern are chlorpyrifos per se and a single metabolite, pyradinol (3,5,6-trichloro-2-pyridinol). Residues of these 2 compounds are measured separately.

Chlorpyrifos was determined using method ACR 84.4 (2) submitted with this petition. A sample of the raw agricultural commodity is shaken with acetone, centrifuged, and the volume is reduced using a Snyder column. The solution is diluted with water and cleaned up on a Sep-Pak  $C_{18}$  cartridge. Chlorpyrifos is eluted from the cartridge with methanol, diluted with water, and extracted into hexane. Analysis is accomplished by GLC using a flame photometric detector. Reported sensitivity is 0.01 ppm. Recoveries ranged from 79-109% for fortifications at 0.01-20 ppm. No storage fortification data were submitted.

Total residues are determined by method ACR 84.4(2), and pyridinol residues are determined by difference, chlorpyrifos being measured in the method above. A sample of the RAC is heated in 10% NaOH in methanol, cooled, shaken and filtered. The filtrate is diluted to volume with methanol and evaporated to near dryness. Following addition of dilute acid, the solution is cleaned up on a Sep-Pak C18 cartridge, and the residue is eluted with methanol. The eluate is diluted with sodium bicarbonate and shaken with benzene. The benzene is discarded, the aqueous layer acidified, and a second aliqot of benzene is shaken with the aqueous layer. Following centrifugation, an aligot of benzene is removed and treated with BSA [N,O-bis(trimethylsilyl)acetamide] to derivatize the residue. Analysis is accomplished by GLC using an electron capture detector. Recoveries using this method ranged from 75-120% at fortifications of 0.05-10 ppm. The reported sensitivity is 0.05 ppm. No storage fortification data were submitted.

Residue data for broccoli, cabbage and mustard greens were submitted with this amended registration request. Based on this residue data for the representative crops for the Brassica vegetables crop group, the submitter wishes to amend registration for the two formulations of Lorsban® allowing foliar application to several Brassica (cole) crop group vegetables including broccoli, Brussels sprouts, cabbage, cauliflower, collards, kale and kohlrabi.

Application of one or both of the formulations, Lorsban® 4E and Lorsban® 50W were made to broccoli. In each trial, 4E was applied once only in the furrow at planting or as a foliar spray, while 50W was applied as a foliar spray for the remaining 3-9 applications. Application rates were 0.75-1.5 1b.a.i./A (0.75X-1.5X max. rate) for 4E and 1 1b.a.i./A (1X) for 50W. In no case does the protocol show applications of 4E within approximately 50 days of sampling (it is not stated when the 4E foliar applications were made). The intervals between the 4-10 total applications were approximately 7 days in most cases. Samples were either composites of 12 individual plants cut with 2-3 inches of stem, or flower heads (5 lbs.) sampled randomly around the field. No storage fortification data were submitted with this amended registration, and the length of time the samples were stored (frozen) was not stated. Uncorrected chlorpyrifos residues per se ranged from 0.02-4.5 ppm (7 day PHI), ND (not detectable)-1.8 ppm (14-15 day PHI) and ND-1.5 ppm (21 day PHI). Total residues ranged from 0.02-5.7 ppm (7 day PHI), ND-2.3 ppm (14-15 day PHI) and ND-1.65 ppm (21 day PHI).

Residue data were also submitted for cabbage. Applications were made at rates of 0.75-1.9 lb.a.i./A (0.75% to 1.9%) for Lorsban® 4E and 1 lb.a.i./A (1%) for Lorsban® 50W; the former being applied once only either at the base of the plant or as a foliar spray, and the latter applied as a foliar spray in all cases. The total number of applications ranged from 5-10. Uncorrected residues of chlorpyrifos per se ranged from 0.02-4.6 ppm (7 day PHI), ND-2.8 ppm (14-15 day PHI) and ND-0.94 ppm (21 day PHI). Corrected total residues ranged from <0.07-6.8 ppm (7 day PHI), ND-5.7 ppm (14-15 day PHI) and ND-2.94 ppm (21 day PHI).

Lorsban® 4E and Lorsban® 50W were applied to mustard greens at rates similar to those described for cabbage. Uncorrected chlorpyrifos residues per se ranged from 0.18-3.5 ppm (7 day PHI) and ND-1.3 ppm (14-15 day PHI). Total residues ranged from 0.48-3.94 ppm (7 day PHI) and ND-1.48 ppm (14-15 day PHI).

Based on data for cabbage and mustard greens, there is little difference in residues for the 4E and 50W formulations.

No residue data were supplied in which low volume sprays (3-5 gallons/A) were utilized. Analysis of the data submitted shows that residues tend to increase as spray volume decreases for broccoli, cabbage and mustard greens. Considering how closely the residues in or on broccoli approach the 2 ppm tolerance, these low volume sprays could cause the tolerance to be exceeded. Therefore, data for low volume spray applications (3-5 gallons/A) should be submitted for representative Brassica (cole) crops.

## Conclusions

- (1) The nature of the residues of chlorpyrifos in plants is adequately understood. The residues of concern are chlorpyrifos per se and a single metabolite, pyridinol (3,5,6-trichloro-2-pyridinol).
- (2) Information on the length of storage of the samples were not submitted with the amended registration request. This data will be required for RCB to determine if the tolerances for brassica crop group vegetables will be exceeded by this new use.
- (3) No data were submitted reflecting low volume (3-5 gallons/A) application of chorpyrifos to brassica crops. Data reflecting low volume application to representative crops will be required before RCB can determine if the brassica crop group tolerance will be exceeded by the proposed new use.

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## Recommendations

RCB recommends against the amended registration at this time.

cc:R.F., Circu, M.Metzger, Chlorpyrifos S.F., Amended use file, PMSD/ISB RDI:E.Zager:EZ:4/1/86:RDS:4/1/86 TS-769:RCB:M.Metzger:MM:Rm810:4/1/86